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# 学位論文内容の要旨

博士 (環境科学)

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## 学位論文題名

### Electrocatalytic Nitrate and Nitrous Oxide Reduction Reactions at Trimetallic Interfaces of Pt, Pd and Sn

(白金, パラジウム, スズの三元金属界面における硝酸イオンおよび亜酸化窒素の電極触媒還元反応)

Nitrate anion ( $\text{NO}_3^-$ ) contamination in groundwater, which is mainly caused by agriculture and industrial effluents, has a negative effect on the environment and human health, such as methemoglobinemia (blue baby syndrome) and human cancer. The electrocatalytic  $\text{NO}_3^-$  removal is the most promising technique, in which  $\text{NO}_3^-$  can be reduced to harmless dinitrogen ( $\text{N}_2$ ) with many by-products: nitrite ( $\text{NO}_2^-$ ), nitric oxide (NO), nitrous oxide ( $\text{N}_2\text{O}$ ), ammonium ion ( $\text{NH}_4^+$ ), and hydroxylammonium ion ( $\text{NH}_3\text{OH}^+$ ).  $\text{N}_2\text{O}$  is a potential by-product, which is accountable for global warming and the depletion of the ozone layer. Therefore, efficient electrocatalysts are needed to develop for both  $\text{NO}_3^-$  reduction reaction ( $\text{NO}_3\text{RR}$ ) and  $\text{N}_2\text{O}$  reduction reaction ( $\text{N}_2\text{ORR}$ ). In the previous studies, Sn-modified Pt and Pd electrodes were widely studied for  $\text{NO}_3\text{RR}$  but the same electrode was not studied for the reduction of  $\text{NO}_3^-$  and its potential by-products:  $\text{NO}_2^-$ , NO, and  $\text{N}_2\text{O}$ . In a reverse system, only Pt nanoparticle (NP)-modified fluorine-doped tin oxide (FTO) substrate electrodes (Pt/FTO) were studied for  $\text{NO}_3\text{RR}$ , in which the Pt/Sn interface catalyzed the reaction. Therefore, the objective of this thesis is to expand the investigation on (i) the reverse system: (Pt+Pd) mixture NP-modified FTO electrodes and (ii) chemically synthesized Pt-Pd-Sn NP electrodes for the reduction of  $\text{NO}_3^-$  and its potential by-products:  $\text{NO}_2^-$ , NO, and  $\text{N}_2\text{O}$ . This thesis includes five chapters. Chapter 1 describes those backgrounds and the objective of this study, and the conclusions were summarized in Chapter 5.

In Chapter 2, the Pt and/or Pd NPs on FTO substrate electrodes: Pt/FTO, Pd/FTO, and Pt/Pd/FTO were prepared by an arc-plasma deposition (APD) method and investigated for the electrocatalytic reduction of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , NO, and  $\text{N}_2\text{O}$  in acidic media by cyclic voltammetry (CV). The trimetallic PtPd/Sn interface of the Pt/Pd/FTO electrode with Pt:Pd = 3:2 atomic ratio showed higher catalytic activity than the bimetallic Pt/Sn or Pd/Sn interface for the  $\text{NO}_3\text{RR}$  and  $\text{N}_2\text{ORR}$ , whereas the PtPd/Sn interface showed no drastic contribution to the electrocatalytic  $\text{NO}_2^-$  and NO reduction reactions. Because the  $\text{NO}_3^-$  and  $\text{N}_2\text{O}$  reduction reactions occur in the potential region of H-adsorption on Pt and Pd electrodes, the PtPd/Sn interface could enhance  $\text{NO}_3^-$  and  $\text{N}_2\text{O}$  adsorption and/or suppress the H-adsorption.

In Chapter 3, Pt–Sn and Pt–Pd–Sn NPs with the optimized Pt:Pd = 3:2 atomic ratio obtained from the APD method were synthesized and investigated for the electrocatalytic N<sub>2</sub>ORR in acidic media by CV. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy dispersive spectroscopy (EDS) mapping images confirmed the formation of Pt@Sn and Pt–Pd@Sn core@shell NPs. The trimetallic Pt–Pd–Sn NPs showed higher N<sub>2</sub>ORR activity than the bimetallic Pt–Sn NPs. The suppression of H-adsorption was confirmed from the lower Faradaic efficiency of H<sub>2</sub> at the PtPd/Sn interface than that at the Pt/Sn interface at 0.0 V vs. RHE, resulting in the high N<sub>2</sub>ORR activity. The PtPd/Sn interface showed turnover frequency (TOF) of  $5.29 \text{ mol}_{\text{N}_2} \text{ mol}_{(\text{Pt}+\text{Pd})}^{-1} \text{ min}^{-1}$  for the N<sub>2</sub>ORR to N<sub>2</sub> with about 100% Faradaic efficiency at +0.06 V vs. RHE.

In Chapter 4, Pd nanocubes (NCs) on carbon support were prepared, modified with Sn, and then studied for the electrocatalytic N<sub>2</sub>ORR in acidic media by CV to understand the role of surface structure at the Pd/Sn interface. TEM images confirmed the preparation of NCs. The Sn modification increases the N<sub>2</sub>ORR activity of NCs. The Sn modification could suppress the H-adsorption at Pd(100) surfaces of the NCs, resulting in the enhancement of the N<sub>2</sub>ORR activity.

In conclusion, it was demonstrated that the enhancement of NO<sub>3</sub><sup>-</sup> and N<sub>2</sub>O adsorption and/or suppression of H-adsorption is necessary at the electrode surface for the improvement of the NO<sub>3</sub>RR and N<sub>2</sub>ORR in acidic media. The trimetallic PtPd/Sn interface can highly modulate such competitive adsorption processes, resulting in the high NO<sub>3</sub>RR and N<sub>2</sub>ORR activity. Furthermore, the Pd/Sn interface of Sn-modified Pd NCs improved N<sub>2</sub>ORR activity more than unmodified Pd NCs through the suppression of H-adsorption. The findings of this thesis will lead to the development of the highly efficient interfaces between Pt–Pd mixture/alloy NPs and Sn or shape-controlled Pt–Pd mixture/alloy NPs and Sn for the modulation of the NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>O, and H-adsorption processes.